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## X-RAY FLUORESCENCE ANALYSIS WITH A FOCUSED PRIMARY BEAM

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The sample to be analyzed is irradiated by a convergent, almost monochromatic X-ray beam (conventional or point-focusing type). In the first method, utilizing an intense line, an X-ray spectrometer is used for recording the X-ray spectra in the usual way. In the second and most promising method, the wavelength of the incident beam is either slightly shorter or slightly longer than the absorption-edge wavelength of the sought element. In the former case, the radiation coming into the counter includes fluorescence radiation; in the latter it does not, and the balance gives, without a spectrometer, the intensity of the fluorescence radiation due to the selected element. This method, which permits analysis of surfaces smaller than a few tenths of a square millimeter, has been applied with success. Some examples of its application (analysis of zinc in ores, determination of the thickness of very thin films of nickel) are given.

Auther

1. Introduction

If a small portion of a given specimen is to be analyzed by means of the conventional X-ray fluorescence analyzer, it is conventional to bundle the

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\*\* Numbers in the margin indicate pagination in the original foreign text.

primary radiation by a narrow slit.

For focusing the X-ray beam on the specimen, it is also possible to make use of the focusing properties of curved crystals. Unfortunately, in most cases, the beam rendered convergent in this manner is also made practically monochromatic, so that what one gains in solid angle might be lost again in energy. For example, let us consider the fluorescence of zinc: In the case of an excitation by a primary polychromatic radiation, the useful wavelength domain lies between the minimum wavelength of this radiation (i.e., 0.27 Å for a potential of 45 kv) and the wavelength of the K absorption discontinuity of zinc (1.28 Å). Thus, this domain extends over a range of about 1 Å. If, conversely, a radiation emitted by a conventional monochromator is used, the passband of this monochromator, for a focus of 0.2 mm, will be of the order of 0.01 Å. It is obvious that the energy yield will only be a few percent. However, the /446 energy loss is not catastrophic in the following cases: 1) if an intense line, selected from the primary radiation spectrum, can be used; 2) if one can do without a spectrometer for analyzing the radiation emitted by the specimen.

## 2. Utilization of an Intense Line

To demonstrate whether the method is at all useful, we selected the K $\alpha$  radiation of copper for exciting a cobalt specimen. The X-ray tube used was a Machlett AEG 50 A tube; the monochromator, of the point-focusing type, was formed by a single-crystal aluminum foil, cylindrically oriented and curved, such that the reflecting planes (200) had a toroidal shape (Despujols, 1952). The principal radii of curvature were 50 and 345 mm, and the useful area of the foil was 5 × 35 mm<sup>2</sup>. The impact area of the beam on the specimen was about 1 mm<sup>2</sup>. Finally, the spectrometer equipped with a curved aluminum crystal (R =

= 250 mm, useful area: 10 × 20 mm) developed by Cauchois et al. (1950) was /447 equipped with an old-type Geiger counter. The specimens, in the form of pellets, were tableted from a mixture of cobalt chloride and potassium chloride (Fig.1).

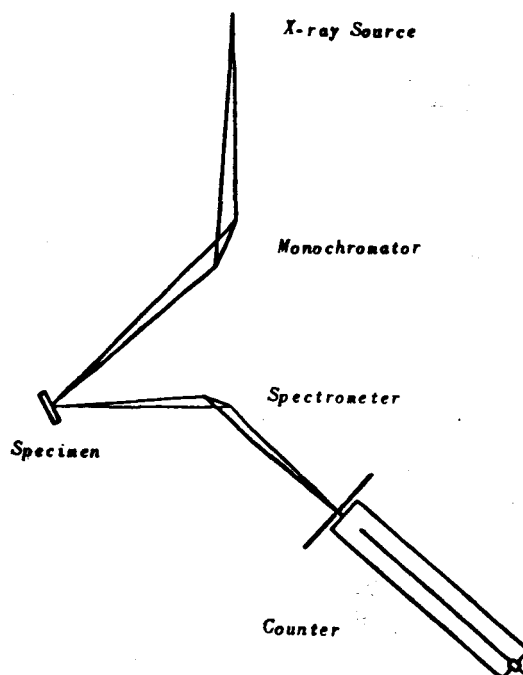


Fig.1 Schematic Diagram of the Device Used for  
Exciting Cobalt by  $K\alpha$  Radiation of Copper

Figure 2 gives a general idea on the results obtained with this first design, for an output of the X-ray tube of 15 ma at 40 kv. It is true that the number of pulses at the exit from the counter is low, but we are confident that we will be able to increase this considerably, by using crystals of larger dimensions and a proportional counter.

One of the advantages of the method resides in the facility with which absorption calculations can be performed, provided that the composition of the matrix is known. In fact, the radiations involved are monochromatic, while the incident and emerging beams make well-defined angles with the surface of the

specimen. In the example given here, the solid curve in Fig.2 gives the result of a calculation based exclusively on the absorption coefficients and on the intensity corresponding to a pellet of pure cobalt (point A).

### 3. Method of Differential Excitation

We developed a method which does not require a spectrometer but necessitates the use of two adjacent wavelengths  $\lambda_1$  and  $\lambda_2$  spanning the wavelength of

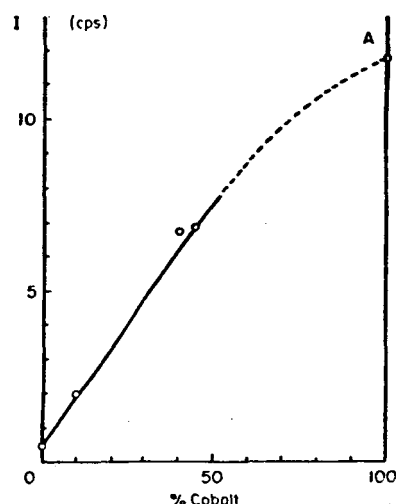


Fig.2 Preliminary Results, Obtained in Exciting Cobalt by the  $K\alpha$  Radiation of Copper

the K absorption discontinuity of the element under study. The primary ra- /448  
diation corresponding to the shortest of these wavelengths can excite the fluo-  
rescence of this element, whereas the other cannot do so. Denoting by  $I_1$  and  $I_2$   
the intensities measured by a counter located in the direct vicinity of the  
specimen, the fluorescence intensity will be given by  $I_1$ , corrected by  $I_2$ .

In the arrangement designed by one of us (H.Roulet), shown in Fig.3, a  
monochromator with single curvature (aluminum crystal, reflection 200) was  
placed in front of the window of a Machlett AEG 50 T tube with a tungsten anode.  
A movable slit cuts out the wavelengths  $\lambda_1$  and  $\lambda_2$  while the object stage and /449

the counter are displaced together with the slit (Roulet and Despujols, 1961).

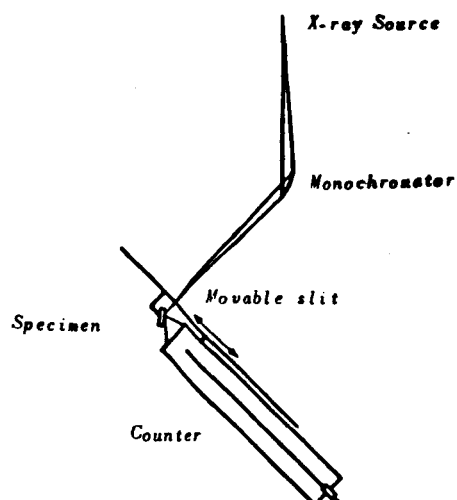


Fig.3 Schematic Diagram of the Device Used for Differential Excitation of Zinc

Figure 4 gives the results obtained for zinc, in a mixture of natural minerals; the dimensions of the window were  $0.5 \times 0.5 \text{ mm}^2$ . The wavelength  $\lambda_1$

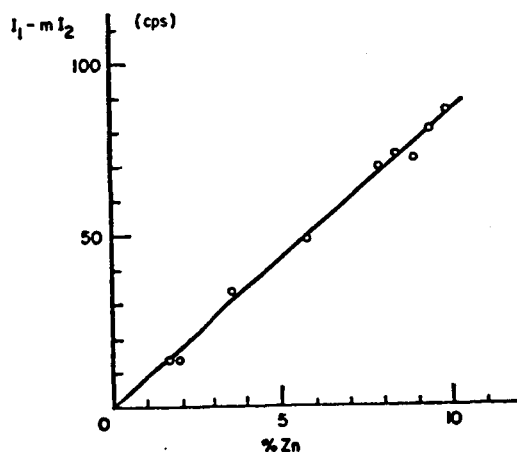


Fig.4 Preliminary Results Obtained for the Differential Excitation of Zinc

corresponded to the  $L\beta_1$  line of tungsten. Despite this fact, the magnitude of the correction coefficient  $m$  was only 3.5 ( $m$  can be readily determined; for zero zinc content,  $m = I_1/I_2$ ).

Still other applications of this method are possible, specifically the measurement of thin films, with or without base. Experiments have also been made on nickel coatings of thicknesses between 250 and 1500 Å, yielding coherent results, with the intensity of fluorescence being proportional to the thickness.

#### 4. Conclusions

A comparison of Figs. 2 and 4 gives a general idea on the intensity gain due to the elimination of the spectrometer, although it is quite difficult to make an accurate allowance for these two factors. The intensity gain was evaluated by a direct measurement in the case of cobalt and was found to be of the order of 500.

It should be emphasized again that these preliminary tests were made with experimental equipment, subject to numerous modifications. However, such as they are, they have demonstrated that X-ray lenses, using curved crystals, may constitute valuable aids in local analyses by X-ray fluorescence. One might even think of a future development of "X-ray probes" which, without actually replacing them, could complement the valuable instruments known as "electron probes".

#### 5. Acknowledgment

This study was entirely based on work and suggestions by Miss Y. Cauchois, Professor at the Faculty of Sciences (University of Paris), Director of the Physical Chemistry Laboratory. We wish to express our gratitude for all advice and encouragement received from this collaborator.

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